High Energy Density Lithium/Sulfur Batteries for NASA and DoD Applications

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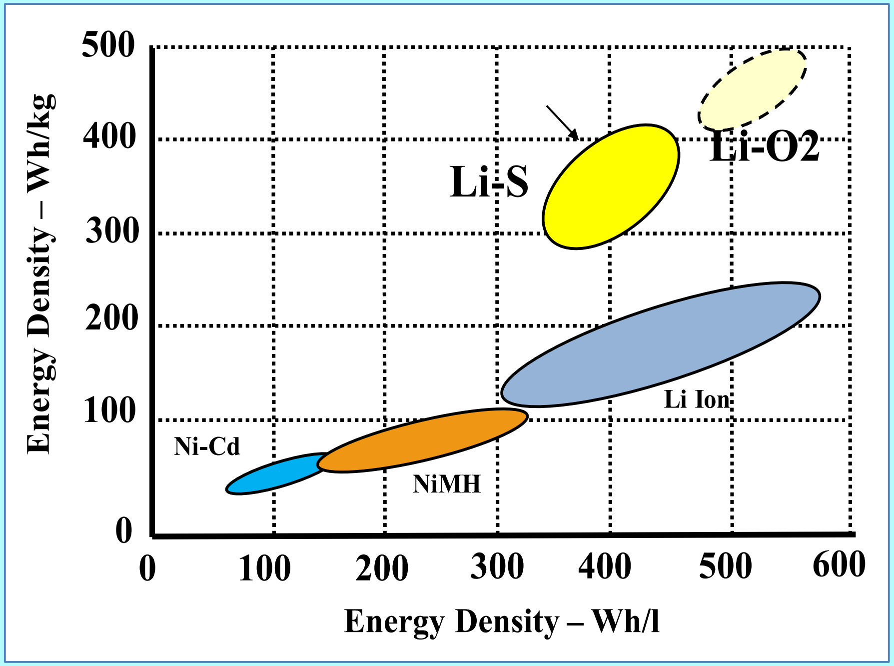
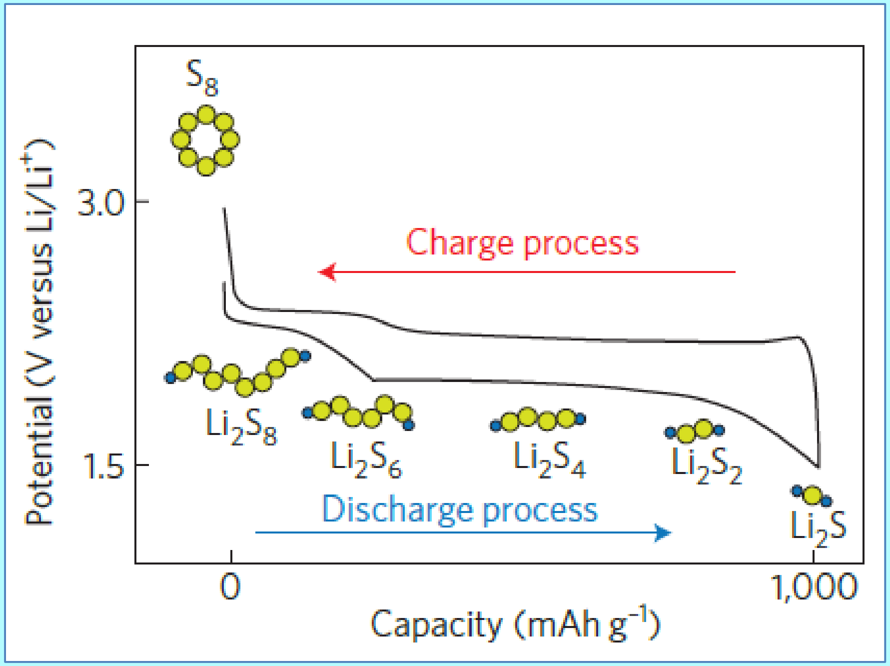
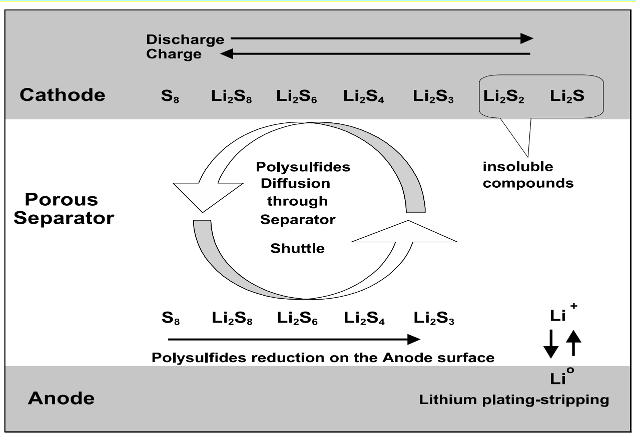
Why Lithium-Sulfur Batteries?

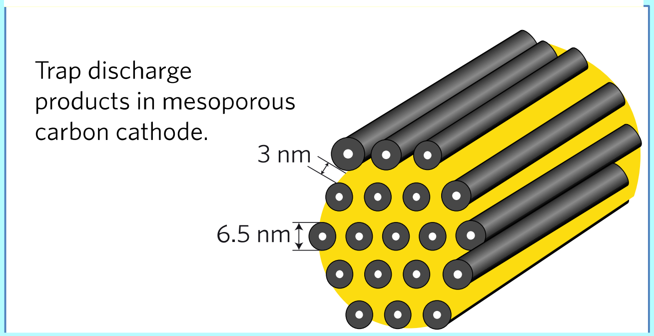




- High specific capacity of 1670 mAh/g;
- High theoretical specific energy of 2567 Wh/kg
- Inexpensive and Environmentally benign
- Abundant in the Earth's crust
- 250-400 Wh/kg realized in practical cells.
  - Higher specific energy cells have generally shorter cycle life

Problems with Li-S and Mitigation Strategies





- Anode passivation and dendrite formation.
- Sulfur expands by 79%
- Poor conductivity of S and its discharge products.
- Polysulfides are soluble in many solvents : Form Redox shuttle and insulating layer (Li_2S) on the anode

Problems	Strategies Adopted	Rationale
Poor cyclabaility and dendrites	Coat with protecting layer (solid electrolyte)	Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites
	Coat with protecting layer (gel polymer)	
Polysulfide dissolution, redox shuttle behavior	Immobilize in carbon host matrix	Strong S-C interactions trap sulfides (e.g. as S_n^{x-} chain-like species, as cyclo-S_8 allotrope does not fit inside pores)
	Use sulfide (discharge product) as cathode	Allows use of non-Li anodes
Poor Conductvity and expansion	Meso/microporous carbon support for S	High electronic conductivity of C mitigates poor S conductivity
Passivation	Use sulfide (discharge product) as cathode	Allows use of non-Li anodes
Soluble sulfides affecting anode stability and performance	Organic electrolyte with additives (e.g. $LiNO_3$, P_2S_5)	Good conductivity, additives react preferentially with sulfide species and passivate Li surface, depassivate cathode
	Ionic liquid electrolyte	Sulfides are insoluble in certain ionic liquids
	Solid-state electrolyte	Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites

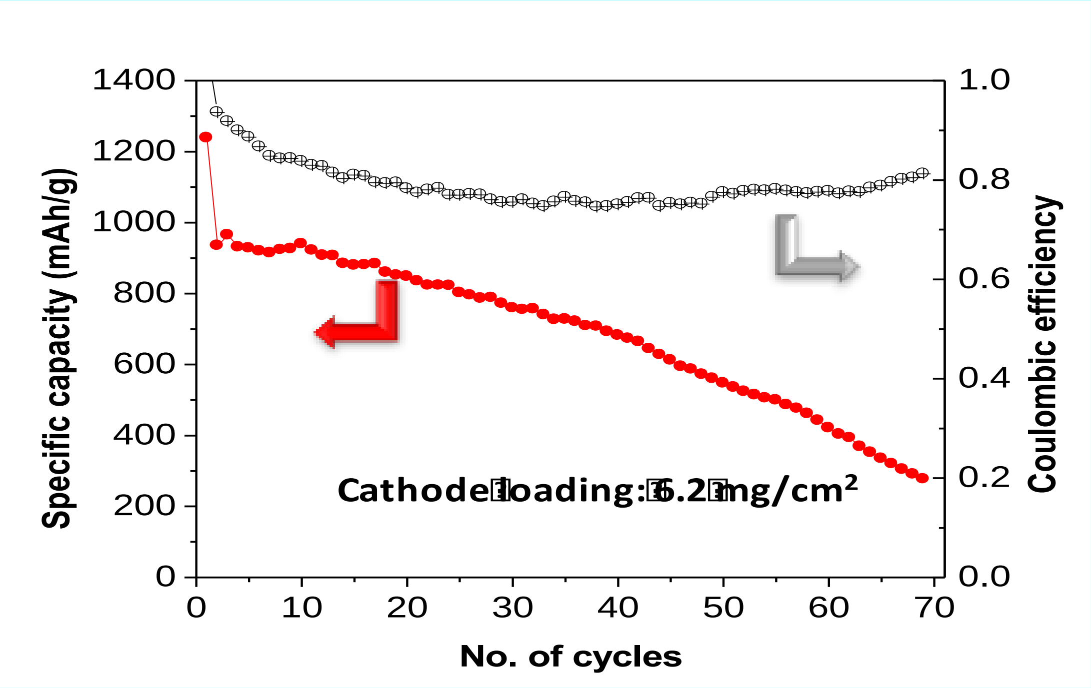
- Some of these approaches have shown improved cycle life, but only with low sulfur loadings

Sulfur cathode With High Loadings for a 400 Wh/kg Li-S cell

- High cathode loadings required for high energy cells
  - High energy Li-ion cells have cathodes (nickel cobalt aluminum oxide, NCA) with a loading of 15 mg/cm^2, i.e., ~8.7 mWh/cm^2 per side of the electrode.
  - For a specific energy of 400 Wh/kg, we will need 1.5 times the specific energy compared to Li-ion cells, i.e., 13 mWh/cm^2 per side.
  - With a voltage of 2.1 V for Li-S cell, this implies an areal capacity of ~6.2 mAh/cm^2 for the sulfur cathode.
  - With 800 mAh/g from sulfur (and with a composition of 65% sulfur), the required loading is 12 mg/cm^2.
  - Almost all reports of Li-S cells in the literature describe performance of sulfur cathodes with a low loading of < 5mg/cm^2 (mostly 2-3 $mg.cm^{-2}$) and/or with low proportion of sulfur in the cathode.
- Electrolyte content needs to be reduced to 4-5 ml/g (currently 9-13 ml/g)

Performance of a S cathode with high Loading in a Li-S cell

1.0MLiTFSI+DME+DOL(95:5) with 0.2 M $LiNO_3$ with a Carbon Cloth



Coat carbon ink on Al foil → Vacuum dry → Coat cathode → Oven dry (no vacuum) → Punch electrodes (coin or pouch)

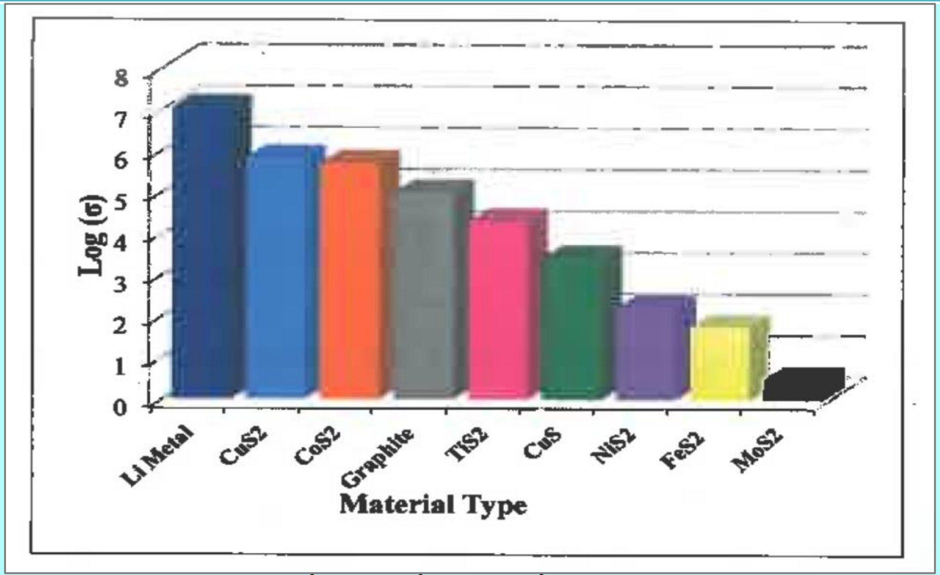
Slurry: sulfur + carbon black + PVDF in NMP → Speed mixer → Coat cathode

- Lower capacity and utilization of sulfur in thicker cathode even with carbon cloth interlayer and $LiNO_3$.
- With a denser sulfur cathodes, more polysulfides are expected to dissolve in the electrolyte.

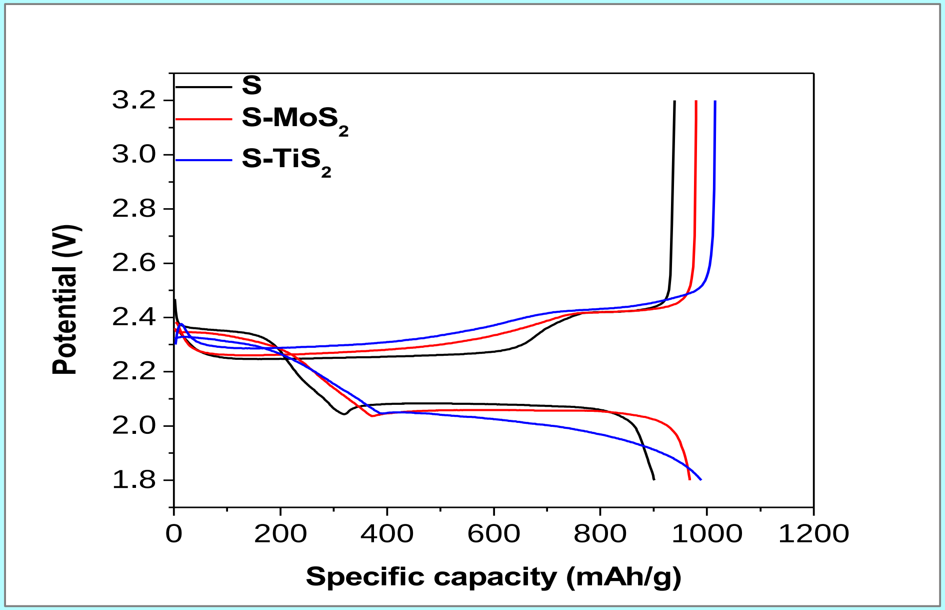
High Areal Capacity S Cathodes

- Transition metal sulfide undergoes reversible reactions around the same voltage range and can add to the cathode capacity and also mediate the sulfur redox reaction.
- Metal sulfide provides some electronic/ionic conductivity and can replace a portion of the carbon.
  - Easier to make dense electrodes with the metal sulfide additions in place of carbon.
- TiS_2 (Manthiram and Cui et al) , VS_2, ZrS_2 (Cui et al) with low loadings (<5mg/cm^2), CuS_2 (Takeuchi et al)

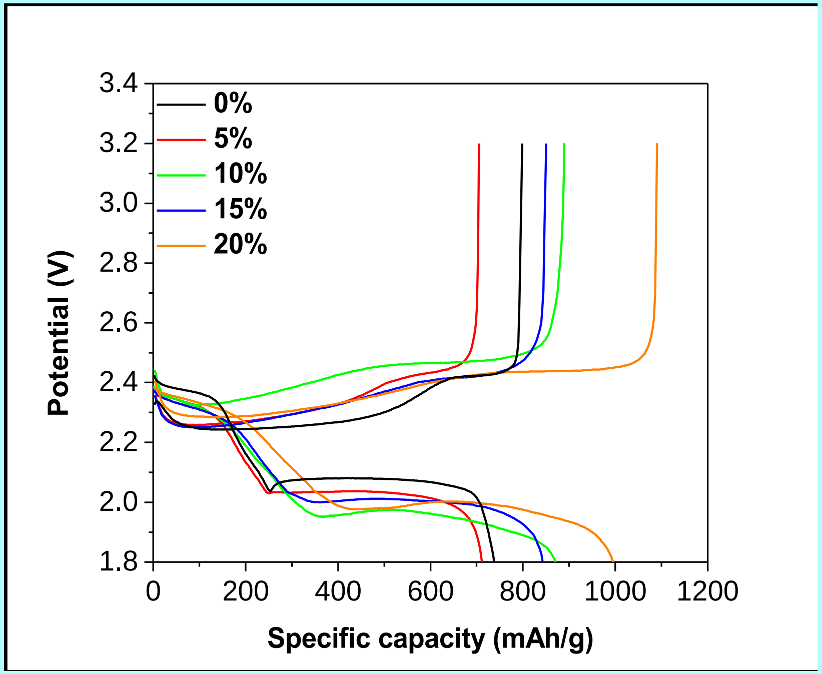
- Screened several sulfides : TiS_2, MoS_2 have shown to be beneficial

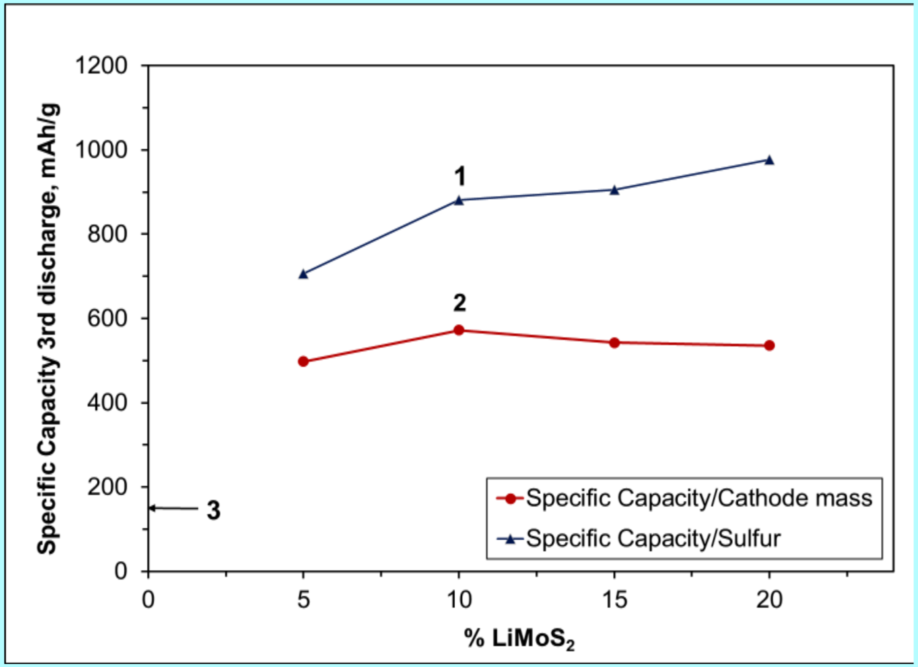


Takeuschi et al DoE Report



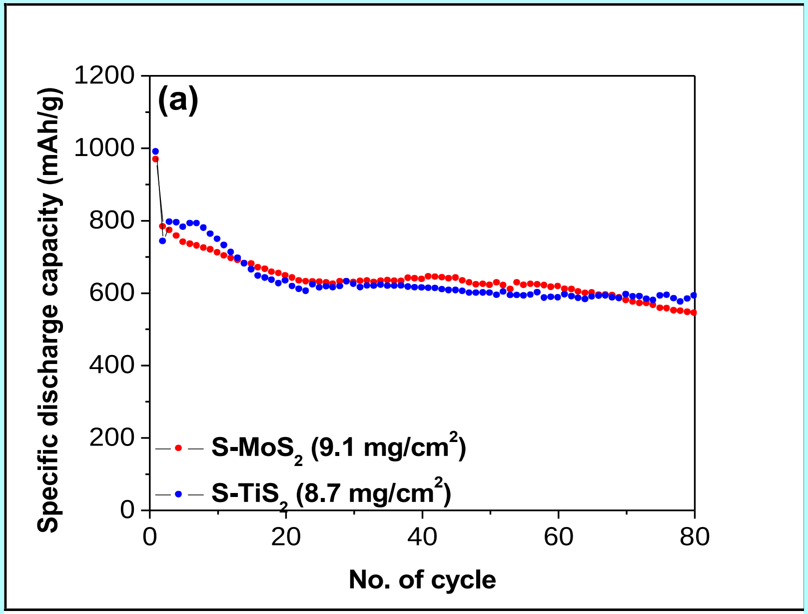
Sulfur Cathode With Different amounts of MoS_2

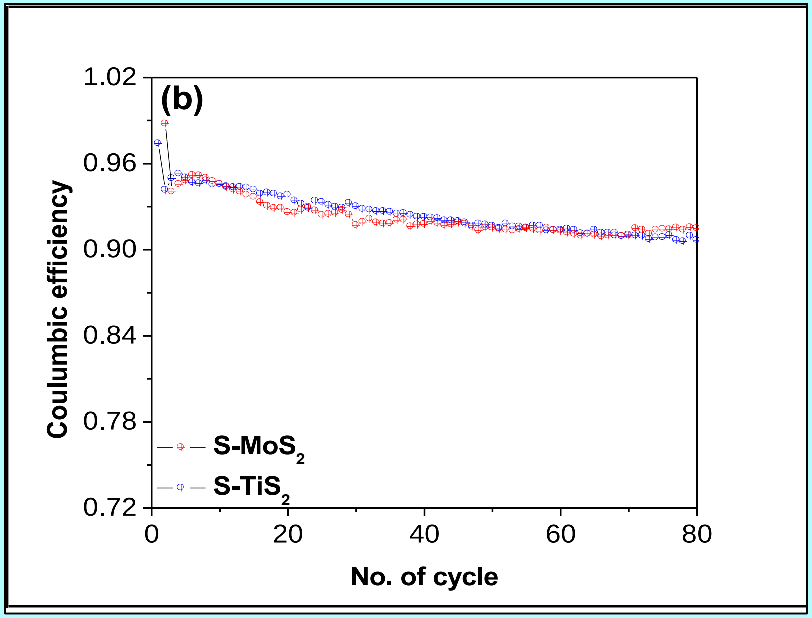




- Three times the capacity per gram of cathode material compared to Li-ion cathode powder (NCA)
- Specific capacity of sulfur increases with MoS_2 loading, but specific capacity of total cathode does not

Sulfur blended with MoS_2 and TiS_2 (15w%)

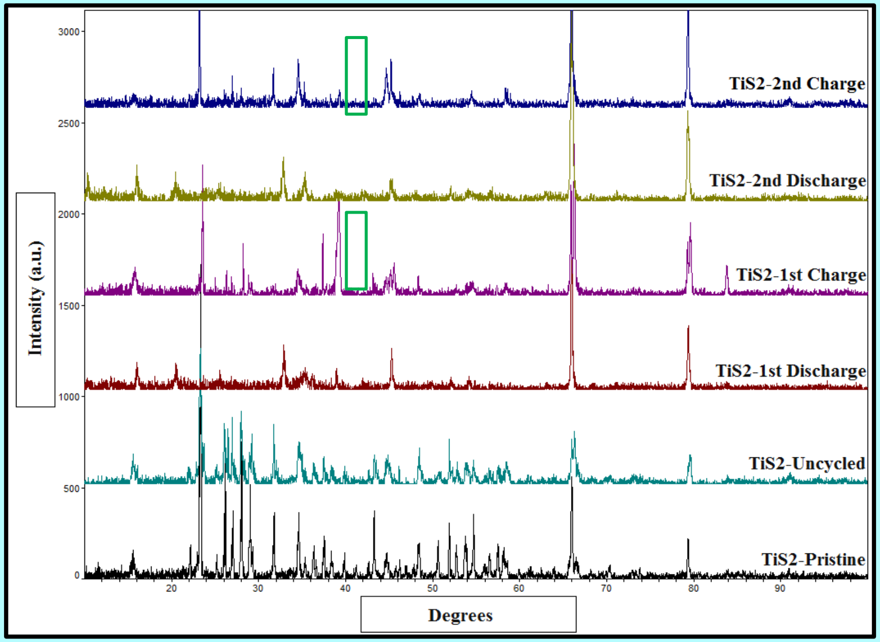




- Good performance considering the high cathode loading and high proportion of sulfur (4.6 mAh/cm^2 per side)
- High coulombic efficiency suggests polysulfide trapping.

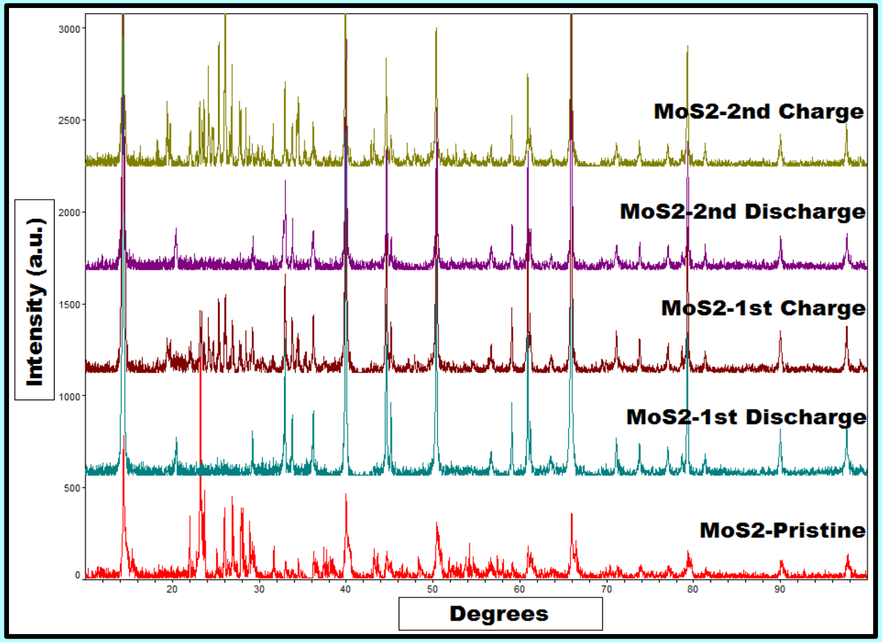
X-ray Diffraction (XRD): TiS_2 - Blended Sulfur Cathode

TIS_2-Blended Sulfur



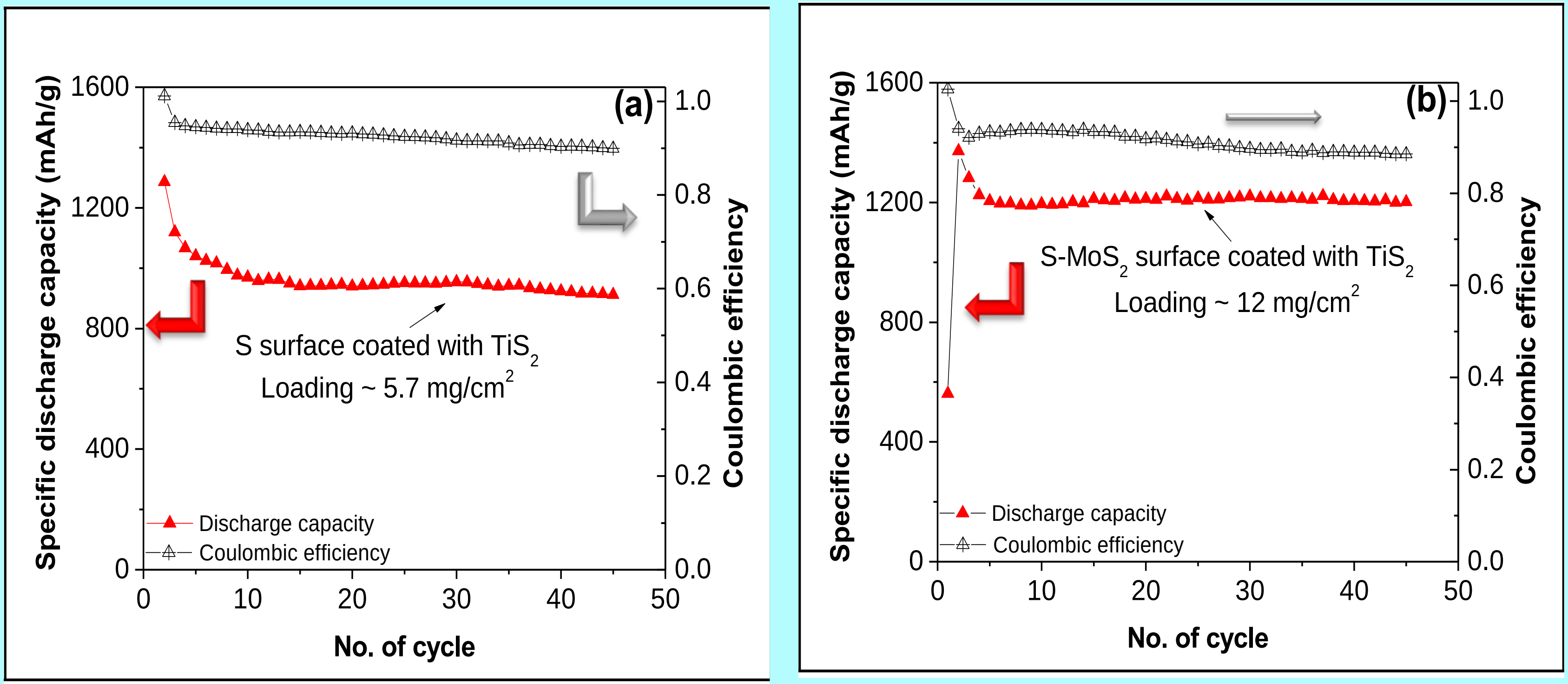
- Blue shades ~ Al foil contribution; Red Shades ~ $LiTiS_2$; Green shades ~ TiS_2
- The XRD spectra for TiS_2 electrodes showed a transition from TiS_2 to $LiTiS_2$ after discharge and transition from $LiTiS_2$ to TiS_2 after charge.

MoS_2-Blended Sulfur

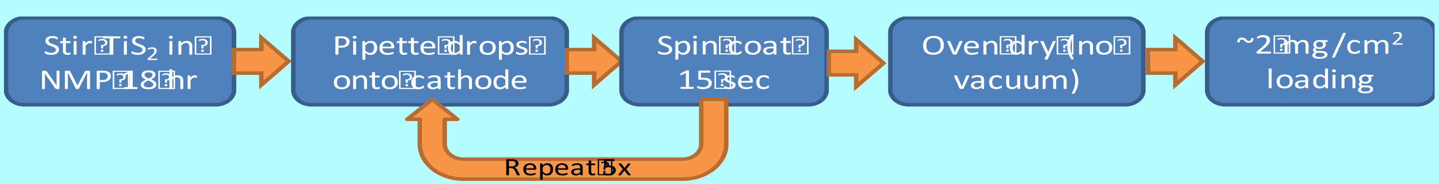


- Blue shades ~ Al foil contribution; Red Shades ~ MoS_2.
- Similar to the baseline and MoS_2 electrodes the S-MoS_2 cathode showed the presence of sulfur peaks after charging and disappearance of the same peaks after discharging.
- No change in the MoS_2 peaks

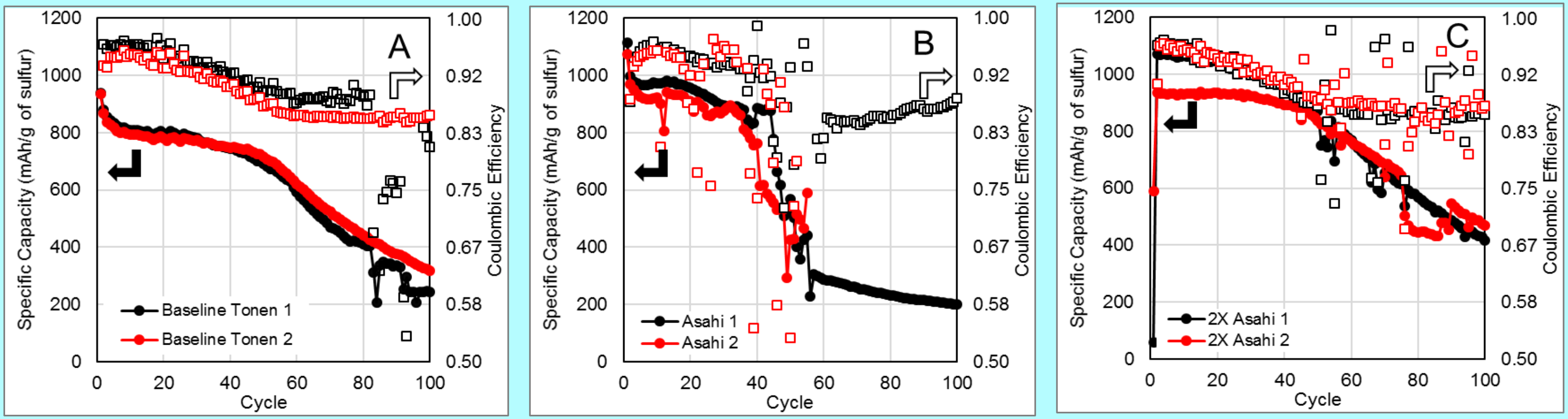
Metal Sulfide Coating as Polysulfide Blocking Layer



- Cycling performance of a conventional sulfur improves with a coating of TiS_2.
- The sulfur cathode blended with MoS_2 and coated with TiS_2 shows a high specific capacity (~1200 mAh/g) relative to S and good cycling stability even with an overall material loading of ~13 mg/cm^2. A portion of this capacity is contributed by TiS_2.

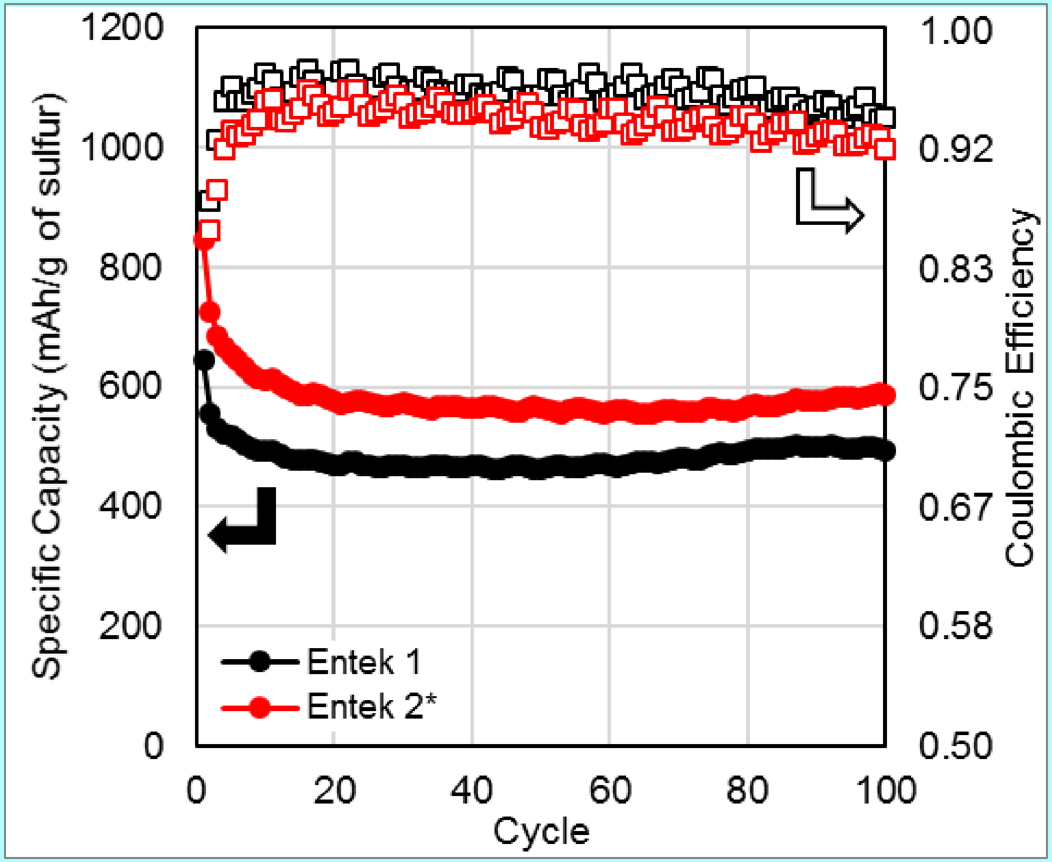


Li-S cells with Al_2O_3-coated separator (Asahi)



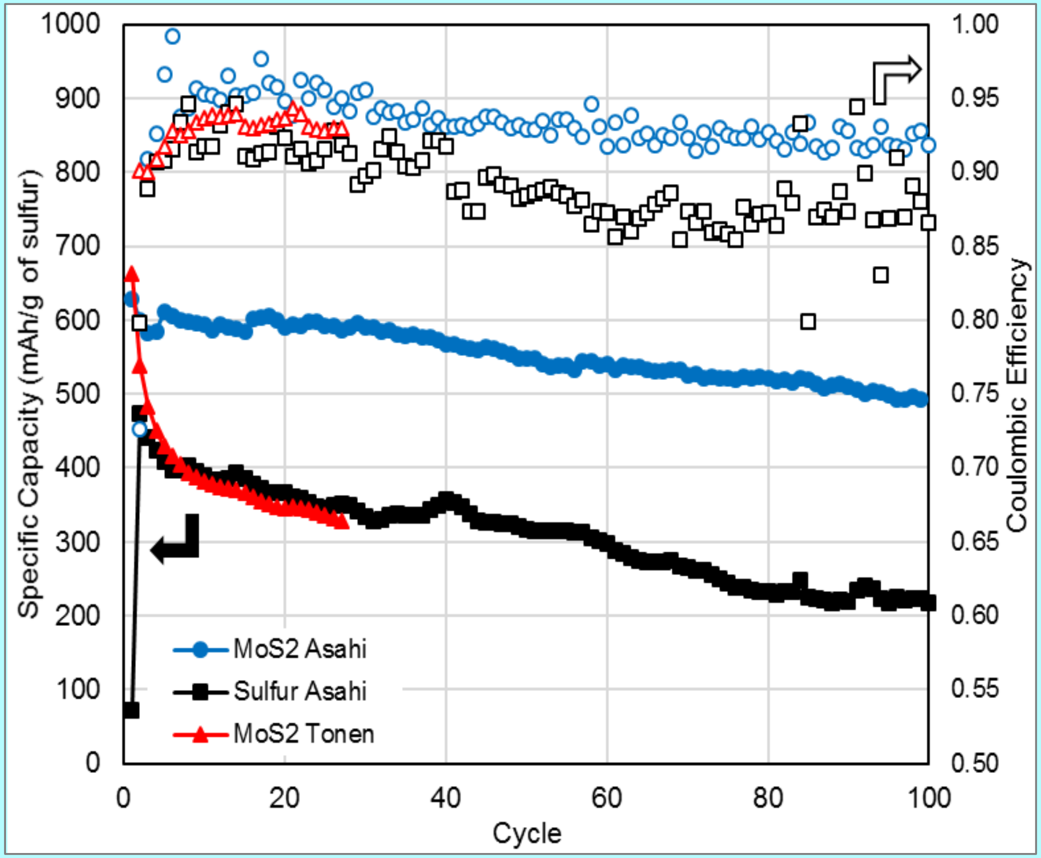
- Separator coated with Al_2O_3 on one side (typically used on the cathode side)
- Improved performance with two layers of separator

Li-S cells with Al_2O_3-coated separator (Entek)



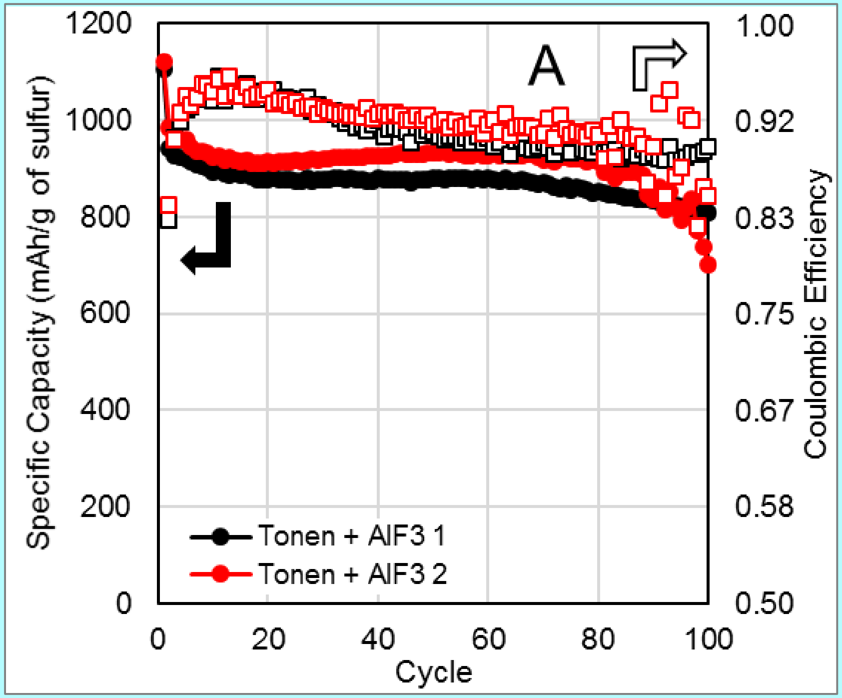
- Separator coated with Al_2O_3 on both sides
- Lower capacity but stable during cycling

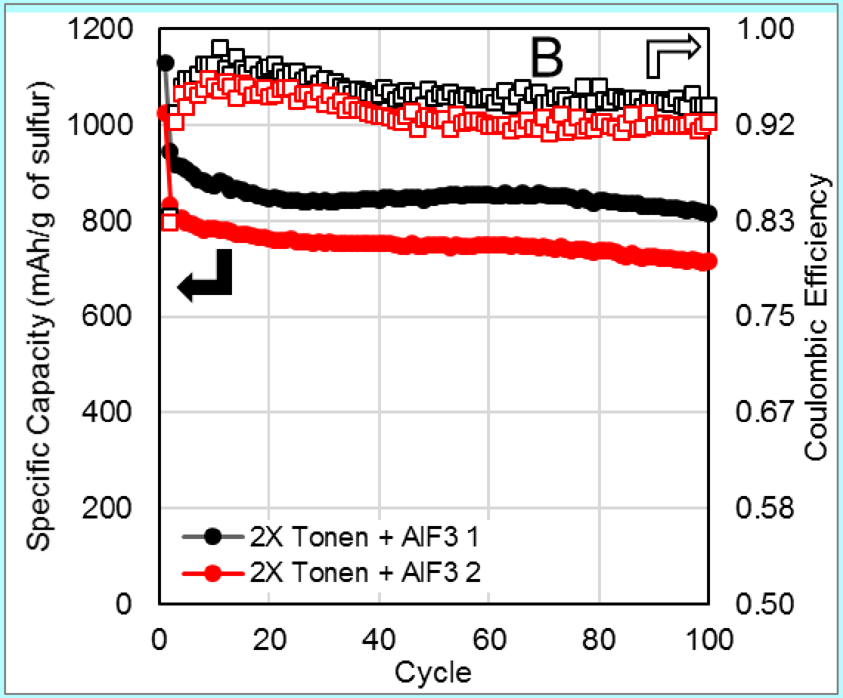
Li-S pouch cells with Al_2O_3-coated separator (Asahi)



- Improved performance with Al_2O_3-coated separator and MoS_2-blended sulfur cathode

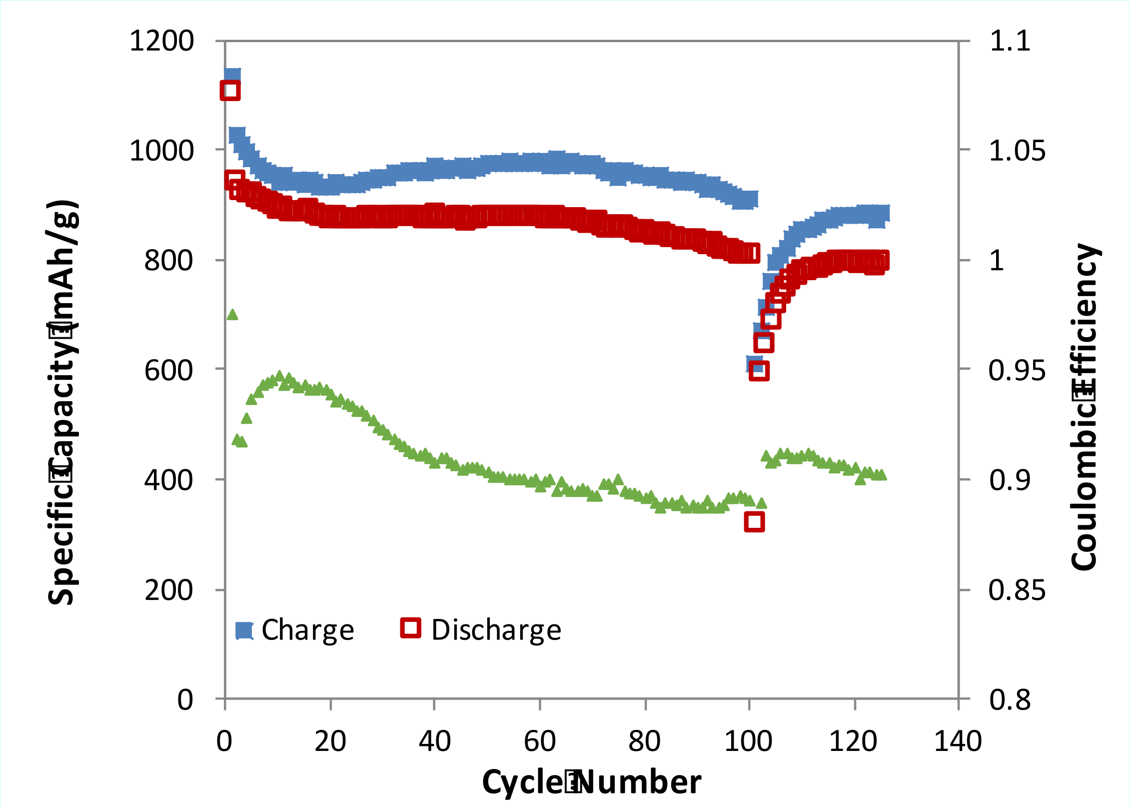
AlF_3-coated Tonen separator (spray coated)





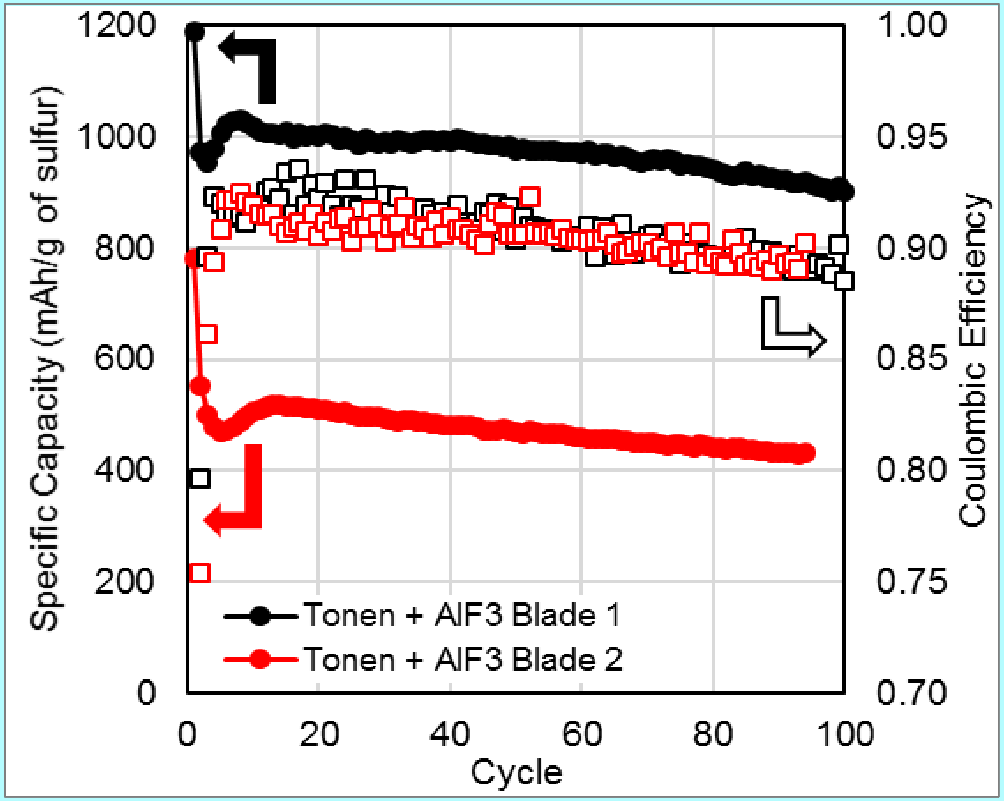
Li-S coin cells containing sulfur cathode of composition S:CB:PVDF(55:40:5), 6.45mg/cm^2 and AlF_{3-}coated Tonen separator (spray coated)

AlF_3-coated Tonen separator (spray coated)



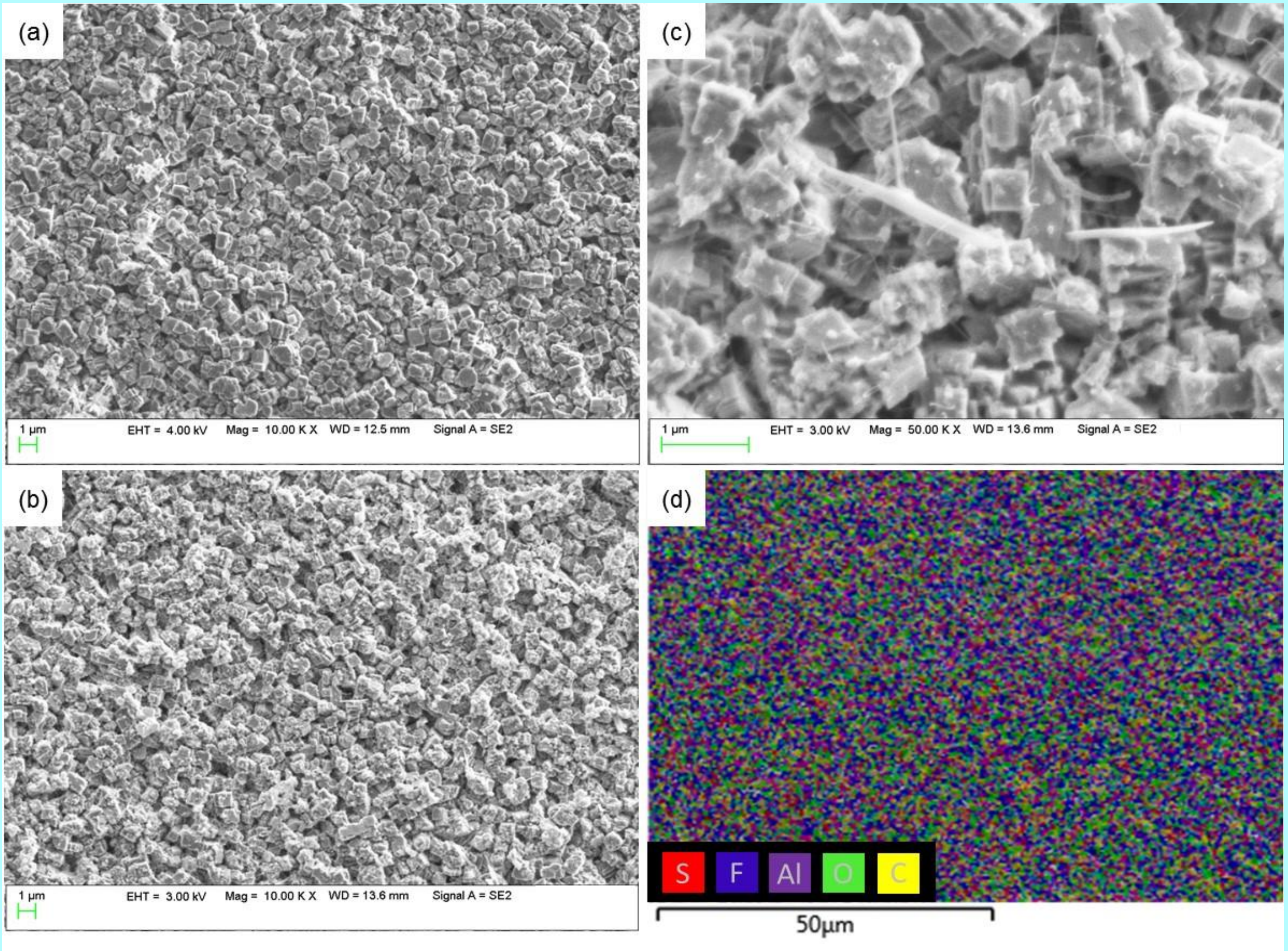
Cycling of Li-S coin cells containing sulfur cathode of composition S:CB:PVDF(55:40:5), 6.45mg/cm^2 and AlF_3-coated Tonen separator (spray coated) – Cell cycling resumed after 100 cycles

AlF_3-coated Tonen separator (Doctor-blade) –Two Layers



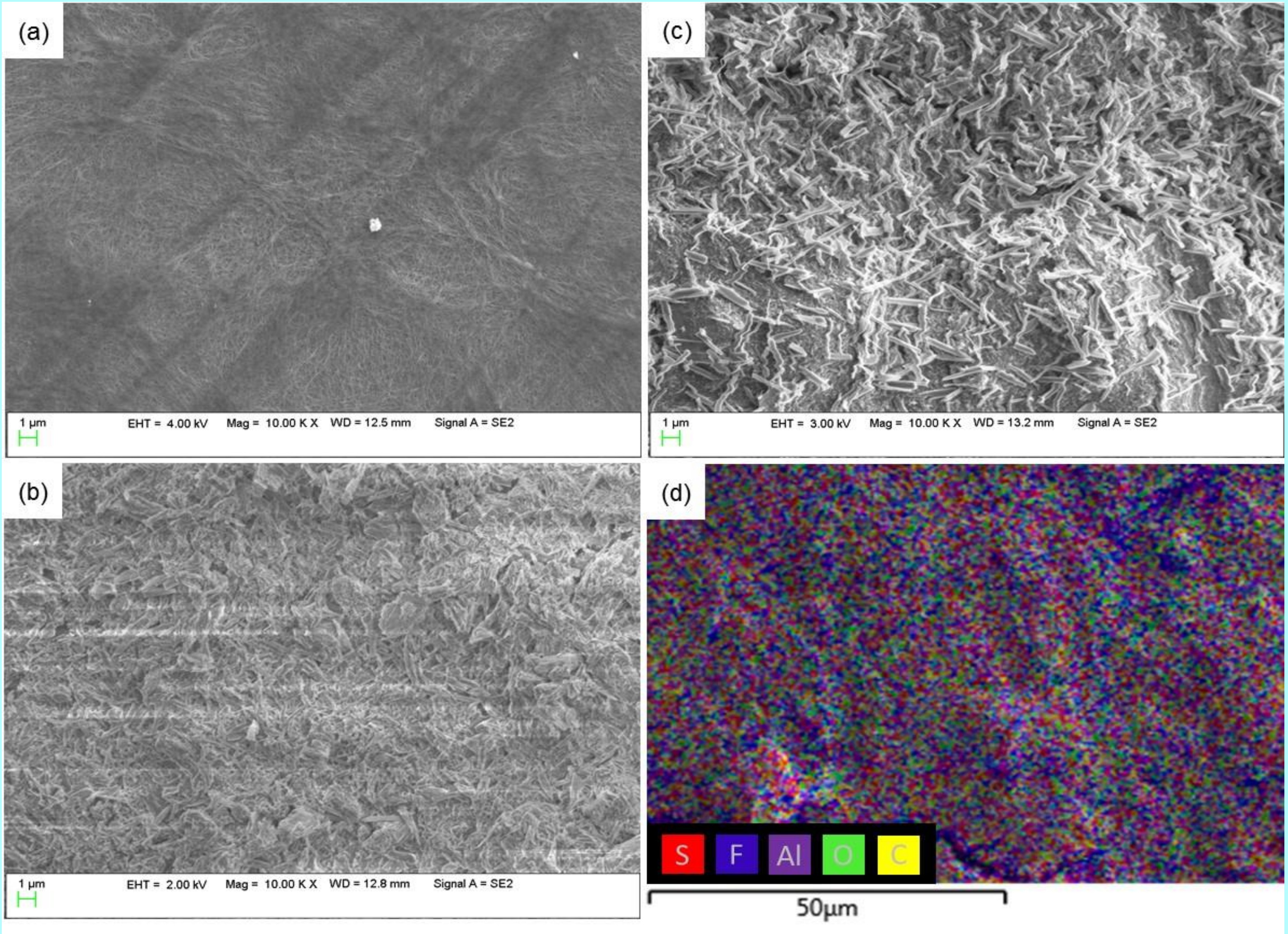
Li-S coin cells containing sulfur cathode of composition S:CB:PVDF(55:40:5), 6.45mg/cm^2 and AlF_{3}-coated Tonen separator (doctor-blade coated)

Asahi Separators from Cycled Cells



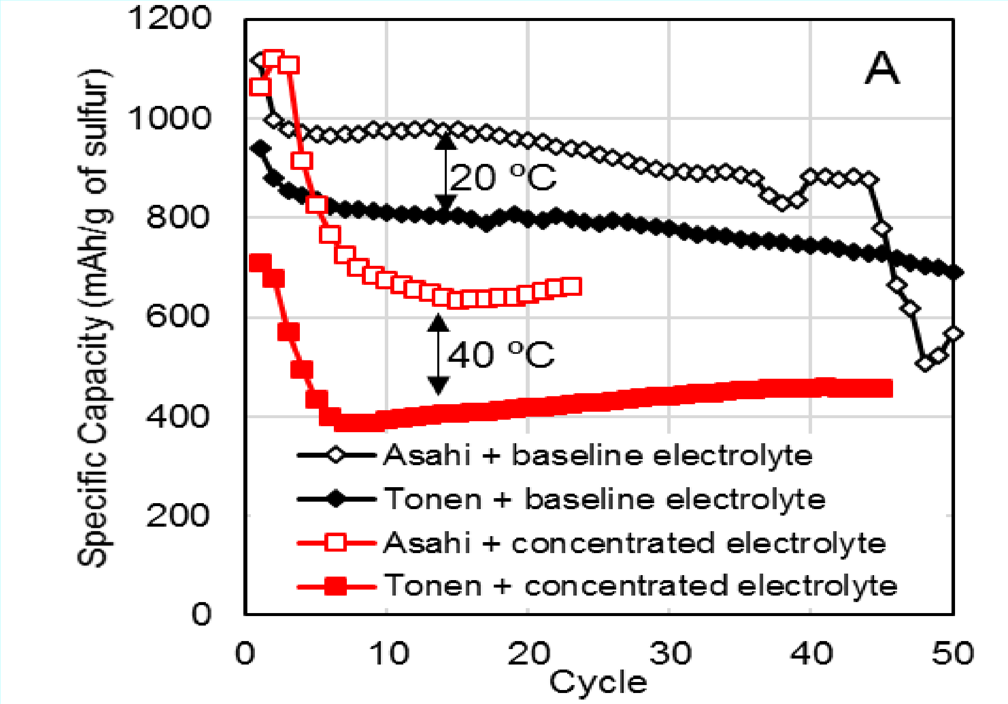
Scanning electron microscopy (SEM) images of (**a**) fresh Asahi separator, (**b**) and (**c**) Asahi separator after 55 cycles showing Al_2O_3 particles present on the surface and deposition of sulfur-containing species on the surface of these particles after cycling. Energy-dispersive spectroscopy (EDS) in (**d**) indicates approximately uniform distribution of sulfur-containing species across the surface of the separator.

AlF_3-coated Separators from Cycled Cells



SEM images of (**a**) fresh Tonen separator, (**b**) Tonen separator coated with AlF_3 and (**c**) AlF_3-coated Tonen separator after 100 cycles showing AlF_3 material present on the surface after coating, and deposition of sulfur-containing species on the surface of these particles after cycling. EDS in (**d**) indicates approximately uniform distribution of sulfur-containing species across the surface of the coated separator.

Concentrated Electrolytes



- Highly concentrated electrolytes (solvent in salt) reportedly prevent Li dendrites on the anode and polysulfide shuttle on the cathode.
- Poor performance observed at room temperature in 4M-7M solutions (poor conductivity)
- Slightly improved performance at 40°C with interestingly high coulombic efficiency. May be an option for low power long-life applications.

Liumin Suo, Yong-Sheng Hu, Hong Li, Michel Armand and Liquan Chen, "A new class of Solvent-in-Salt electrolyte for high-energy rechargeable metallic lithium batteries", NATURE COMMUNICATIONS | 4:1481 | DOI: 10.1038/ncomms2513 | www.nature.com/naturecommunications

Summary

- Novel sulfur/metal sulfide (TiS_2 and MoS_2) and sulfur composite cathodes display high capacity of ≥800 mAh/g (based on sulfur content), high coulombic efficiency and good cycle life (>75% retention through 100 cycles of 100% depth of discharge) at C/3 rate.
  - High cathode loadings (12 mg/cm^2 or ~6 mAh/cm^2 per side) were demonstrated in Li-S cells containing composite cathodes with good utilization
  - Result in a high specific energy of 400 Wh/kg in prototype cells.
- Metal sulfide coatings also improve the cycle life by minimizing the polysulfides in the electrolyte.
- New separators with ceramic coating (Al_2O_3 and AlF_3) offer interesting opportunities for further improving this technology. They will augment the composite sulfur cathodes.

Acknowledgements

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